PB86-194230

Sulfate Mobility in Acid Soils and Implications with Respect to Cation Leaching: A Review

Florida Univ., Gainesville

Prepared for

Corvallis Environmental Research Lab., OR

May 86

U.S. Department of Commerce
National Technical Information Service
NTIS

PB86-194230

EPA/600/D-86/094
May 1986

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EPA/NSU APP-0273-1983

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U.S. ENVIRONMENTAL PROTECTION AGENCY
CORVALLIS, OR 97333

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TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA/600/D-86/094	2.
3. RECIPIENT'S ACCESSION NO. PB86 194230/AS	
4. TITLE AND SUBTITLE Sulfate Mobility in Acid Soils and Implications with Respect to Cation Leaching: A Review	5. REPORT DATE May 1986
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) L.A. Gaston, R.S. Mansell and R.D. Rhue	8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Soil Science Dept University of Florida Gainesville, FL 32611	10. PROGRAM ELEMENT NO.
	11. CONTRACT/GRANT NO. EPA/NCSU APP-0273-1983
12. SPONSORING AGENCY NAME AND ADDRESS Environmental Research Laboratory Office of Research and Development U.S.Environmental Protection Agency Corvallis, OR 97333	13. TYPE OF REPORT AND PERIOD COVERED Symposium paper
	14. SPONSORING AGENCY CODE EPA 600/02

15. SUPPLEMENTARY NOTES

Project officer: R.G.Wilhour FTS 420-4634

16. ABSTRACT

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Since sulfuric acid is commonly present as a major component of orthopogenic acid precipitation, sorption of sulfate anions can beneficially limit accelerated leaching of basic cations as well as mobilization of aluminum in soils with large contents of Fe and Al oxides. Extensive sulfate sorption essentially limits soil acidification processes to that portion of the soil profile above the advancing front of sorbed sulfate.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT Release to Public	19. SECURITY CLASS (This Report) Unclassified	21. NO. OF PAGES 21
	20. SECURITY CLASS (This page) Unclassified	22. PRICE

EPA Form 2220-1 (9-73)

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ABSTRACT

Relative to a non-sorbing (conservative) solute, sulfate is generally less mobile in soils. Factors that affect sulfate mobility are 1) solution concentration of sulfate, 2) time of contact between sulfate solution and sorbent, 3) temperature, 4) solution pH, 5) other ionic species present, and 6) type of sorbent. These factors are discussed with reference to several pertinent experimental studies. Sorption mechanisms and studies of sulfate movement in soils are discussed as well.

Since sulfuric acid is commonly present as a major component of orthopogenic acid precipitation, sorption of sulfate anions can beneficially limit accelerated leaching of basic cations as well as mobilization of aluminum in soils with large contents of Fe and Al oxides. Extensive sulfate sorption essentially limits soil acidification processes to that portion of the soil profile above the advancing front of sorbed sulfate.

[1] Contribution from the Institute of Food and Agricultural Sciences, University of Florida, Gainesville. This work was supported in part by the United States Environmental Protection Agency under project No. A0457-06. However, this manuscript has not been subject to Agency Review and no official endorsement should be inferred.

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INTRODUCTION

The mobility of sulfate in soils is important inasmuch as the leaching loss of sulfate may produce nutritional stress in crops. Also, sulfate mobility may affect the leaching losses of nutrient cations from a soil subjected to inputs of sulfuric acid in acid precipitation (Johnson et al., 1979 and Singh et al., 1980).

Sulfate movement is determined by the combined effects of convective and diffusive-dispersive transport and sorption-desorption processes. For one-dimensional transport, reversible sorption-desorption, and steady water flow, the convective-dispersive transport equation for sulfate is given by

$$\frac{\partial C}{\partial t} + \frac{\rho \partial S}{\theta \partial t} = D\frac{\partial^2 C}{\partial x^2} - v\frac{\partial C}{\partial x} \qquad [1]$$

where C is solute concentration in solution, S is concentration in the sorbed phase, θ is volumetric water content, ρ is soil bulk density, D is the hydrodynamic dispersion coefficient, $v = q/\theta$ is the pore water velocity, q is the Darcy water velocity, x is distance, and t is time.

The greater the extent of sulfate sorption, the greater is the retardation of sulfate movement relative to a non-sorbing solute. Several factors influence the quantity of sulfate sorbed per unit mass of sorbent as well as its time rate of change. These are 1) the concentration of sulfate in the soil solution, 2) the time of contact between sulfate and the sorbent material, 3) the temperature at which sorption occurs, 4) the solution pH, 5) the nature of other ionic species present, and 6) the nature of the sorbent. Each is sequentially discussed below.

Equilibrium Sorption Isotherms

Sorption isotherms for sulfate have been interpreted to conform

either to the Langmuir or the Freundlich equations. The Langmuir equation may be written as

$$S/b = \frac{kC}{1 + kC} \qquad [2]$$

and the Freundlich equation as

$$S = KC^n \qquad [3]$$

where C is solute concentration, S is concentration in the sorbed phase, b is the sorption maximum and k, K, and n are constants. Mansell and Selim (1981) have discussed assumptions and limitations of equations [2] and [3] for describing phosphate movement in soil.

Data of Kamprath et al. (1956) for sulfate sorption on a Cecil soil at constant pH were described by the Langmuir equation. The sorption maximum was reached at 400 g m^{-3} of S as SO_4^{2-} in solution. Aylmore et al. (1966), Hansan et al. (1970), and Couto et al. (1979) investigated sorption on, respectively, pseudoboehmite and hematite, several Hawaiian soils, and surface and subsurface materials from two Oxisols and an Alfisol. They concluded that the Langmuir equation was applicable for describing sulfate sorption by these soils.

Chao et al. (1962b) concluded that the Fruendlich equation better described their sulfate sorption data for four soils than did the Langmuir equation. No sorption maximum was observed for solution concentrations up to 500 g m^{-3} of S as SO_4^{2-}. Bornemisza and Llanos (1967) were able to describe sulfate sorption on three Costa Rican soils using the Freundlich isotherm. Singh (1984a) found that the Freundlich equation gave the best fit to sorption data for two iron-podzols, a semipodzol, and a brown earth.

In some studies, neither equation described the date.

Aylmore et al. (1966) observed that the sorption isotherms for two kaolin clay minerals exhibited two plateaus. Each sorption region on the isotherms was described by the Langmuir equation. These authors interpreted sulfate sorption to occur at two sets of energetically-different sorption sites. Rajan (1978) found that sulfate sorption on hydrous alumina yielded a curvilinear isotherm, and that sorption decreased with increasing solution concentration of sulfate beyond about $280\ g\ m^{-3}$ sulfate.

Less research has been performed to develop isotherms for desorption than for sorption of sulfate. Aylmore et al. (1966) found that the sulfate desorption isotherms for pseudoboehmite and hematite showed marked hysteresis with respect to the corresponding sorption isotherms. Rajan (1979) suggested that apparent non-singularity for the isotherms was due to a failure to maintain constant pH during desorption; and, by controlling the pH during desorption, the author demonstrated reversible sulfate sorption on a natural allophane, Te Aketea, for which previous results had indicated irreversibility. Sanders and Tinker (1975) presented evidence that sulfate sorption is reversible over short periods but not over periods of several days. Selim et al. (1976) showed that nonsingular sorption-desorption isotherms may also result when contact periods are insufficient to establish true chemical equilibrium.

Effect of Contact Time Upon Sorption of Sulfate

If the time period for contact between sorption sites and a moving stream of sulfate solution is inadequate to obtain equilibrium,

the extent of sulfate sorption decreases and sulfate mobility increases. Substantial evidence suggests that sulfate sorption is a time-dependent process.

Sanders and Tinker (1975) found no measureable change in solution sulfate concentration between 1/2 hour and 4 hours reaction times for sorption on a sandy loam. Rajan (1978) reported that sulfate sorption on hydrous alumina was about 90% complete within 10 minutes of contact time. Equilibrium was not reached, however, until 3 hours of reaction time. Chang and Thomas (1967) found that sulfate sorption occurred over several days for two Cecil soils and a Georgia kaolinite coated with iron oxide. Barrow and Shaw (1977) found that the removal of sulfate from solution, availability of sulfate to plants, and extent of desorption each decreased with increased contact time. Singh (1984c) has described the time dependence of sulfate sorption for B horizon material of a Typic Udipsamment and a Typic Dystrochrept using both two-constant rate equations and multiple-order rate equations.

Effect of Ambient Temperature Upon Sulfate Sorption

That sulfate sorption should be affected by changes in reaction temperature is known from chemical thermodynamics. The nature of this effect has been investigated by Barrow and Shaw (1977) and by Singh (1984c). These authors showed that sulfate sorption increases slightly with increasing temperature for temperatures near ambient.

Effect of Solution pH Upon Sulfate Sorption

Kamprath et al. (1956) found sulfate sorption to increase with decreasing pH. This finding is supported by the work of Ensminger (1954), Chao et al. (1963 and 1964), Koter et al. (1971), Scott (1976), Elkins and Ensminger (1971), and Couto et al. (1979). Such

behavior is consistent with the increase in positive sites for anion adsorption as pH decreases. Adsorption may, according to Rajan (1978 and 1979), also occur at neutral sites.

Effect of Competitive Sorption by Other Anions Upon Sulfate Sorption

The presence of any competitively sorbed anion would be expected to affect the extent of sulfate sorption. Ensminger (1954) and Kamprath et al. (1956) showed that the presence of phosphate decreases sulfate sorption. Chao (1964) investigated the effects of several inorganic and organic anions upon sulfate sorption. Phosphate, molybdate, fluoride, arsenate, selenate, oxylate, and tartarate were the most effective in reducing sulfate sorption. Arsenite, silicate, and nitrate were the least effective. The effects of these anions on sulfate sorption extended over a range of pH from 4 to 6. Chang and Thomas (1963) and Gebbart and Coleman (1974) demonstrated that chloride is poorly competitive with sulfate. Barrow found that the competitive effect of phosphate was pH-dependent. The more acidic the soil, the less favored phosphate was over sulfate.

Chao et al. (1963) demonstrated that sulfate sorption is also affected by the species of cation present. With respect to the sulfate salt used, sorption decreased according to the sequence, $CaSO_4$, K_2SO_4, $(NH_4)_2SO_4$, Na_2SO_4. With respect to type of cation-saturated soil, sorption decreased according to the sequence, Al-soil, unaltered soil, Ca-soil, K-soil, Na-soil, NH_4-soil. Cationic effects were less marked than the effect of pH. The authors suggested that cationic effects could be due either to the formation of a bridging complex in which a trivalent or divalent cation links sulfate

to a negative exchange site or reduced anion repulsion when the diffuse double layer contains trivalent or divalent cations.

Effect of the Nature of the Sorbent on Sulfate Sorption

Among inorganic sorbents, aluminum and iron oxide materials and kaolinitic minerals exhibit the greatest affinity for sulfate. Ensminger (1954) found that dehydrated Al_2O_3 sorbed more sulfate than did iron oxide or hydrous oxides. Kaolinite was intermediate in sorption capacity. Kamprath et al. (1956) found that two soils dominated by 1:1 clays and aluminum and iron oxides sorbed more sulfate than did a soil dominated by 2:1 clays. Chao et al. (1962a) found that soils exhibiting the greatest sulfate sorption were highly weathered, with appreciable free aluminum and iron oxides and exchangeable aluminum. Chao et al. (1962c) demonstrated that removal of aluminum or iron oxides from sulfate-retentive soils reduced sulfate sorption. A similar effect was shown by Singh (1984b) for an iron-podzol. Chao et al. (1964) also coated poorly retentive soil material with aluminum- or iron-oxides. Sulfate sorption increased with the number of such coatings. Aluminum-oxide coated soil material sorbed more sulfate than did iron-oxide coated soil material. Sorption studies by Koter et al. (1971) showed that sulfate sorption was greater the more aluminum and iron-oxides the sorbent material contained. Singh et al. (1979) observed greater sulfate sorption by the subsurface soil of a Tropept than by the surface soil. The content of extractable aluminum and iron was also greater in the subsurface material. For a Calcic Cambisol, Sanders and Tinker (1975) ascribed sulfate sorption to the presence of particles containing

hematite and magnetite. Haque and Walmsley (1973) found initial sulfate content and sulfate sorption significantly correlated ($P < .05$) to extractable aluminum oxides but not to extractable iron oxides.

There is a general lack of agreement about the effect of organic matter on sulfate sorption. Chao et al. (1962c) removed organic matter from sulfate retentive soils by H_2O_2 oxidation and observed a reduced capacity of these soils to sorb sulfate. Koter et al. (1971) found that peats sorbed more sulfate than several other sorbents, including Fe_2O_3 and kaolin. Haque and Walmsley (1973) found that levels of native sulfate in soils from Trinidad or St. Vincent were significantly correlated ($P<.01$) to organic matter content. Singh et al. (1979) attributed the greater sulfate sorption exhibited by surface material of an Andept, compared to that shown by subsurface material, to the higher organic matter content of the surface soil.

In opposition to these findings, Singh (1984b) found that removal of organic matter from an iron-podzol and a brown earth did not reduce sulfate sorption. Couto et al. (1979) and Johnson et al. (1979) found that, for soil samples of similar mineralogy, samples containing more organic matter sorbed less sulfate than did samples containing less organic matter. The results from a study by Johnson and Todd (1983) suggested that organic matter had a negative effect on sulfate sorption by surface soils and by B horizon soil material of Spodosols and podzolized soils.

Sulfate Sorption Mechanisms

Much work has been done to elucidate the mechanism of sulfate sorption in soils. Harward and Reisenaur (1966) reviewed sulfate

retention mechanisms. These include 1) coordination with aluminum or iron in oxide materials via displacement of coordinated water or hydroxyl and a similar exchange on the edges of 1:1 type clays, 2) a mechanism whereby sulfate and cation are both retained (termed "molecular adsorption") and 3) precipitation reactions.

Chao et al. (1965) and Bornemisza and Llanos (1967) showed that solution pH increased with sulfate sorption. This result was interpreted to indicate hydroxyl release from coordination sites upon sulfate adsorption. Hingston et al. (1967 and 1972) proposed that water is displaced from positive sites in this "specific adsorption" process. The observed pH increase reflected the tendency of sulfate adsorption to shift the zero point of charge to more acid values. In a study of sulfate adsorption on allophanes, Rajan (1979) presented evidence for sulfate ligand exchange for hydroxyl. According to the author, for small quantities of sulfate adsorbed, sulfate is adsorbed as a binuclear bridging complex with the displacement of water or hydroxyl-ions from adjacent metal atoms. For greater quantities of sulfate adsorbed, sulfate appeared to be adsorbed as a monodentate ligand preferentially displacing hydroxyl. For hydrous alumina, Rajan (1978) found sulfate adsorption to proceed with the formation of only the binuclear bridging complex. Parfitt and Smart (1978) presented infrared spectroscopic evidence that sulfate is adsorbed onto goethite, akaganite, lepidocrocite, hematite, and amorphous ferric hydroxide as a bidentate ligand. Their overall reaction for sulfate adsorption, analogous to that proposed by Rajan (1978, 1979), is

$$\begin{matrix} Fe\text{---}OH \\ Fe\text{---}OH_2^+ \end{matrix} + SO_4^{2-} \longrightarrow \begin{matrix} Fe\text{---}O \\ Fe\text{---}O \end{matrix}\!\!>\!S\!<\!\begin{matrix} O \\ O \end{matrix} + H_2O + OH^- \qquad [4]$$

Conceptually, (Harward and Reinsenaur, 1966), molecular adsorption may be considered as concurrent specific adsorption and cation exchange. As proposed by Chang and Thomas (1963), this mechanism entails the hydrolysis of an adsorbed acidic cation, allowing for the adsorption of sulfate co-ion and ligand exchange of sulfate for hydroxyl. Since the neutralization of released hydrogen and hydroxyl drives the reaction, the hydrolytic cation adsorption reaction cannot be considered uncoupled from the sulfate-specific adsorption reaction. This mechanism, therefore, represents the molecular adsorption of a sulfate salt.

Another form of molecular adsorption is the physical entrapment of sulfate salts in soil micropores. Soils likely to so sequester sulfate include: Ando soils, soils with high aluminum and iron contents, and soils containing pumice (Harward and Reisenaur, 1966).

Several authors have suggested that, while sulfate is adsorbed by a host of materials, it may also be removed from solution in the presence of these materials by precipitation reactions. This is particularly true of precipitation as basic aluminum sulfates. Singh and Brydon (1969), Singh and Miles (1978), and Adams and Hajek (1978) showed that sulfate may be precipitated as basaluminite, $Al_4(OH)_{10}SO_4 \cdot 5H_2O$, or alunite, $KAl_3(OH)_6(SO_4)_2$. Adams and Rawajfih (1979) found comparable soil solution concentrations of sulfate, aluminum, and hydroxide to those of a saturated solution of basaluminite after K_2SO_4 was added to a sandy loam. Wolt (1981) concluded that alunite and either gibbsite or kaolinite may be controlling the soil solution concentration of sulfate for several soils in the Copper Basin of Tennessee. Khanna and Beese (1978),

however, could not demonstrate whether basaluminite or alunite, if either, was controlling the concentration of sulfate in solution. Also, Gebbardt and Coleman (1974) found the solution concentrations of sulfate, aluminum, and hydroxide for the B horizon material of an Andept upon additions of sulfuric acid to reflect a range from supersaturation to undersaturation with respect to basaluminite.

On the basis of these six factors affecting sulfate sorption, general conclusions can be made about sulfate mobility. For example, sulfate movement in a soil dominated by 2:1 clays at a pH near neutrality would be considerably greater than for a soil composed of 1:1 clays or aluminum oxide materials, and with a distinctly acidic pH. Quantitative predictions of sulfate mobility for constant sorbent composition require precise knowledge of the effects of pH and other ionic solutes on the sorption behavior of sulfate so that equation [1] may be appropriately applied. Studies treating sulfate movement have not attempted quantitative predictions by such modelling. These have instead interpreted results in terms of the general effects of pH, competitive sorption by other anions, and the nature of the sorbent materials. The results of these studies are discussed below.

Sulfate Movement

Chao et al. (1962a) studied the leaching-induced movement of surface-applied sulfate in columns of fifteen different soil series from Oregon. The movement of sulfate was least in those soils which were highly weathered, acidic, and contained appreciable amounts of aluminum and iron oxides. Extremes of movement were exhibited by the highly weathered Aiken and slightly weathered Deschutes series. After application of 20 /cm of water, the maximum concentration of sulfate in

the column of Aiken series soil was located at about the 5-cm depth; whereas the maximum in the column of Deschutes soil was located at about the 41-cm depth.

Swoboda and Thomas (1965) found that the B2 horizon material of the Cecil series retained surface-applied sulfate against leaching (up to 526 cm of water applied), but that a mixture of Yolo series soil and cellulose did not. The Cecil material was predominantly kaolinitic, and the Yolo material was predominantly montmorillonitic.

Bornemisza and Llanos (1967) leached columns of A and B horizon material of a latosol, a regosol, and an alluvial soil formed from pumice. These soil materials were intermixed with either $(NH_4)_2SO_4$, K_2SO_4, $Ca(H_2PO_4)_2 \cdot H_2O$ and $CaSO_4$ or triple superphosphate. Surface-applied radioactive sulfate was readily leached in the regosol, but little of this sulfate (after 51 cm of applied water) moved from the point of application in the latosol and alluvial soil unless the soil had been amended with phosphate. Sulfate distributions were similar for A and B horizon materials of all soils, except that the B horizon material of the oxidic latosol retained sulfate against leaching, even in the presence of phosphate. The entrapment of sulfate salts by pumice was advanced as the cause of limited sulfate movement in the alluvial soil.

Khanna and Beese (1978) showed that pulse application of chloride and nitrate to columns of an acid podzolic brown soil saturated with sulfate did not desorb sulfate. Previously cited studies have shown that chloride and nitrate have little effect on sulfate sorption.

In a study by Haque and Walmsley (1974), surface-applied sulfate was leached to greater depth in a Mollisol than in an Andept. Limited

movement of sulfate in the Andept was attributed to the higher organic matter content and lower pH of this soil material.

Singh et al. (1980) investigated the effect of simulated acid rain on the movement of sulfate in an iron-podzol and a semipodzol. Surface-applied radioactive sulfate was leached to a greater depth in columns of the semipodzol than in the iron-podzol. This difference in sulfate movement was attributed to the slightly higher pH and lower content of aluminum in the semipodzol.

Johnson et al. (1979) estimated sulfate fluxes with incoming precipitation, at the soil surface and at several depths below the surface, in both a tropical and a temperate forest. They found that sulfate was accumulating at the tropical site but was near steady state at the temperate site. This difference in sulfate dynamics was attributed to the higher aluminum and iron oxide content of the tropical forest soil.

A Relationship Between Sulfate Sorption and Cation Leaching During Acid Precipitation

Sulfate in the soil solution undergoes sorption under a range of environmental conditions. Highly weathered, acidic soils exhibit a large capacity to sorb sulfate and retain it against leaching. Reduced mobility of sulfate decreases the potential for the development of a crop deficiency of this nutrient and affects the extent of leaching loss of nutrient cations when a soil is exposed to the effects of acid precipitation. Forest soils can be acidified by infiltrating acid rain (Johnson et al., 1982) without being leached of aluminum and basic cations if the anion of the acid is immobilized in the soil. Sulfuric acid is commonly the dominant orthopogenic

component in acid rain. Huete and McColl (1984) have presented evidence of reduced cation leaching from an Alfisol subsoil and an Oxisol surface soil when sulfate, rather than the highly mobile nitrate, is the dominant anion in the acid leaching solution.

Lee (1985) applied sulfuric acid solutions with pH values of 3.0, 3.5, 4.0, and 5.6 for 3.5 yr to large lysimeter boxes containing a sulfate-adsorbing forest soil and either red alder or maple seedlings. Nozzles were used (Lee and Weber, 1982) to apply the simulated rain at a rate of 2.8 (maple) and 3.7 mm h^{-1} (alder) for 3 h d^{-1} and 3d $week^{-1}$ throughout the year. Resulting rain amounts per year were 131 cm for maple and 173 cm for alder. For the maple plots, total annual H^+ deposition was 0.03, 1.3, 4.1, and 13.1 keq ha^{-1} for the pH 5.6, 4.0, 3.5, and 3.0 solutions, respectively. Total H^+ deposition for the pH 3.0 solution was approximately ten times a rate typical of the northeastern U.S.

Decreases in Mg^{2+} and Ca^{2+} concentrations, base saturation, and pH were limited to the uppermost 15 cm of soil and, in most cases, to the pH 3.0 treatment. Concentrations of Mg^{2+} and Ca^{2+} for the pH 3.0 treatments were greater than for the control at a depth of 15 to 30 cm, indicating transport of these cations from the soil surface. The depth at which Mg^{2+} and Ca^{2+} accumulated appeared to coincide with the depth at which SO_4^{2-} was actively being removed from solution by sorption to soil colloids. A sulfate-front had permeated to a depth greater than 20 cm but less than 100 cm.

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